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REASONS FOR TINTING OF CORUNDUM CERAMICS (A REVIEW)

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The reasons and the mechanism of processes responsible for tinting of corundum ceramics are considered in the context of published data. Practical recommendations are issued.

Corundum materials, in contrast to other radioengineering ceramics, have higher mechanical and electric strength, higher resistance to vibration and thermal shocks, low dielectric loss in a wide temperature and frequency interval, and higher resistance to aggressive media and ionizing radiation.

However, in the course of production these materials are more sensitive to impurities contained in the initial materials and to the firing medium, which results in tinting of finished articles. Therefore, production of pure-white corundum ceramics involves certain difficulties. Thus, corundum ceramics in a reducing medium often acquire a gray or even black color, which is attributed to the reduction of oxides and a tarnish resulting from reduced or partly oxidized metals from the heaters and refractory lining of the furnace. In an oxidizing medium, corundum ceramics often acquire a yellow color, which is caused by oxidation of colorant impurities, for instance, iron or titanium (from gray to black), and also formation of lower silicon and aluminum oxides that have a yellowish tint. The gray tarnish and color of corundum ceramics in a reducing medium can be related to evaporation of molybdenum in the form of lower oxides and formation of molybdates, the majority of which have a yellow color in a reducing medium [1].

Therefore, a producer and a customer of corundum ceramics usually agree to consider the color of ceramics as a nonregulated parameter, since the main properties of ceramics virtually do not change, and it is almost impossible to identify the distinctions in ceramic properties using the available methods of industrial enterprises.

This subject calls for serious research involving up-to-date electrophysical analysis methods, since either different sources of materials or technological production specifics can be responsible for tinting of corundum ceramics.

In the present study we attempt to discuss some reasons accounting for tinting in corundum ceramics.

Interatomic bonds in Al_2O_3 are implemented via sp electrons; at low temperatures this material manifests dielectric properties, whereas at temperatures above 1000°C, Al_2O_3 , similarly to CaO , MgO , and BaO , becomes a semiconductor with electron conduction and exhibits high sensitivity to partial pressure at temperatures 1300–1700°C, which is probably determined by splitting off of oxygen atoms and emergence of aluminum ions with lower valence.

Analysis of samples of amorphous and black aluminum oxides show nonstoichiometry, which is related to the location of the aluminum atom in the lattice interstice. The black tint of aluminum oxide is attributed to the aluminum atom in the lattice interstice, and an intense exothermic effect is observed at 790–810°C due to the oxidation of the interstitial aluminum atoms and restoration of stoichiometry in Al_2O_3 [2].

The gray color can also be due to the presence of alumina spinel Al_2O_4 , which corresponds to the formulas $\text{AlO} \cdot \text{AlO}_3$ or $\text{Al}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$. This spinel has been identified in production of electrocorundum and corundum ceramics in a reducing medium, and also in heating a mixture of aluminum oxide and carbon (oil coke) at temperatures 1600–1800°C. This material has a face-centered cubic lattice of the spinel type.

The compositions of spinel can vary depending on the firing temperature: $\text{AlO} \cdot 1.26\text{Al}_2\text{O}_3$ at 1600°C, $\text{AlO} \cdot 1.21\text{Al}_2\text{O}_3$ at 1700°C, and $\text{AlO} \cdot 1.06\text{Al}_2\text{O}_3$ at 1750°C, which was identified by chemical analysis [2]. This spinel is not oxidized even in an oxygen flow at temperature around 1000°C and is resistant to strong acids and alkalis. Some authors ascribe the formula $\text{AlN} - \text{Al}_2\text{O}_3$ to spinel as well (the presence of nitrogen was identified by chemical analysis). It has the same lattice, refraction, and density parameters (but different x-ray interference maxima) [2]. Such a spinel at 1000°C is transformed into corundum $\alpha\text{-Al}_2\text{O}_3$ with a loss of weight by 6.9%.

There also are known lower aluminum oxides Al_2O_3 and AlO with the respective lattice parameters 4.06 and 4.30 Å and solid solutions between them. Other possible compounds

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are aluminum oxycarbides $\text{Al}_4\text{O}_4\text{C}$ and Al_2OC containing up to 4.4% carbon, which are identified by x-ray structural analysis. Carbon can be introduced via an organic binder or transmitted via a gas binder from graphite heaters. These compounds have a light blue or gray tint. Tungsten or molybdenum can influence the reduction of Al_2O_3 .

The lower silicon oxide, mainly monoxide SiO , have colors ranging from yellow and light brown to black-brown and black. The monoxide is formed by heating an equimolar mixture $\text{Si} + \text{SiO}_2$ in vacuum at $1350 - 1500^\circ\text{C}$. This mixture is not dissolved in acids and can be dissolved in hydrofluoric acid only when heated; in 25% NaOH solution it slowly reacts, releasing oxygen, and in a CO_2 and H_2O vapor atmosphere at temperatures $400 - 500^\circ\text{C}$ it is oxidized to SiO_2 .

The monoxide's properties depend on its production conditions. Its structure is not yet clarified; it is stable in an inert medium within the temperature interval $20 - 1000^\circ\text{C}$ and even up to 1200°C . Its oxidation starts at temperatures $300 - 500^\circ\text{C}$ and is accompanied by an increase in weight up to 17% at 1000°C , which corresponds to silicon sesquioxide Si_2O_3 that has a golden-yellow color and a cubic structure. Furthermore, there exists x-ray-amorphous Si_2O_3 and intermediate phase Si_2O_4 (57.6% Si), which slowly oxidizes at room temperature to Si_2O_3 and then to SiO_2 .

The nonstoichiometry of silica is related to its reduction to lower oxides due to dissociation or under the effect of reducing agents. Silicon monoxide is formed in the course of heat treatment or reduction in the form of a surface quasi-phase in the areas of accumulation of point defects and dislocations: SiO_2 .

The Si – O system implies the presence of two eutectics at the temperatures 1270 and 1450°C with atomic content of oxygen 15 and 60%, respectively, and the melting point of silicon monoxide is 1600°C [2].

Consequently, tinting of corundum ceramics may be related to the reduction and oxidation not only of impurities but also of its main oxides which in classical ceramics technology are regarded as stable and without deviations from stoichiometry, i.e., Al_2O_3 , other metal oxides, and SiO_2 .

Due to the application in ceramic technology of vacuum furnaces and furnaces with various media (oxidizing, reducing, and neutral) operating at higher temperatures and the use of various heating elements, it is necessary to pay more attention to redox processes and the processes of surface and volume diffusion. The information concerning these processes can be obtained from publications on the physical chemistry of high-temperature processes and nonstoichiometry of oxides [3, 4].

Stoichiometry of oxides is currently regarded as an exceptional phenomenon: in most cases, oxides are characterized by nonstoichiometry, i.e., a deficit of cations or anions and other defects in the crystal lattice. One of the most stoichiometric oxides is MgO , in which the concentration of cation defects is virtually equal to the concentration of anion defects; however, the cation defects prevail (i.e., there is a

slight but perceptible deficit of the metal). At high temperatures, cation vacancies are the main defects [4].

The formation of these defects and their equilibrium is described using the effective charge concept suggested by Kreger and Wink and currently recommended as the standard concept. The list of point defects is presented in [4], and its application is described in [5], in which it is compared to the list of true charges.

The study in [5] pays special attention to firing and defects of "black ceramics." Of certain interest for ceramic technologists is the study in [6], which discusses the physical and chemical properties of nonstoichiometric oxides widely used in the production of ceramics and refractories.

The effect of impurities, the firing medium, and the structure of corundum materials can be revealed in high-temperature mechanical testing in accordance with OST 4GO.737.200.

The negative effect of iron impurities and corundum materials can be eliminated by a joint introduction of additives ($\text{MgO} + \text{Y}_2\text{O}_3$) in the amount of 0.05 – 3.00%, which makes it possible to eliminate the labor-consuming operation of washing iron off, whose impurities are often present in raw materials and introduced in the course of crushing and milling of the batch components. The joint introduction of magnesium and yttrium oxide additives delays the growth of corundum grains to a greater extent than magnesium oxide by itself. To improve the interphase adhesive characteristics of corundum materials, these additives can be introduced in the form of soluble salts in the amount of 0.05 – 1.50%.

The high-temperature mechanical properties of various corundum materials are investigated in [7].

To synthesize ceramics M-7 (VK-94-2), it may be advisable to use glass of the $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system (35 – 50% SiO_2 , 35 – 45% BaO , and 12 – 20% Al_2O_3) instead of glass of the $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system. The former glass is recommended for sintering of steatite and forsterite ceramics instead of traditional sintering additives [8].

Problems of production of dense corundum ceramics and their behavior in firing are investigated in [9]. It is recommended to add 0.1% triethanolamine for alumina milling, which makes it possible to decrease the milling duration from 24 to 6 h with preservation of the ratio between the granular fractions (with the prevailing grain size less than $2 \mu\text{m}$).

The main effect on the color of corundum is exerted by impurities of silica, sodium oxide, and ferric oxide, which are mainly concentrated in the vitreous phase and in $\beta\text{-Al}_2\text{O}_3$ (i.e., in $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$). The microhardness of gray corundum is 141.9 MPa and that of white corundum is 235.8 MPa; the viscosity of white and gray corundum is almost equal (55 and 56%, respectively), and that of black corundum is 70%.

These oxides are contained either in the form of impurities ($\text{Na}_2\text{O}, \text{Fe}_2\text{O}_3$), or as batch components for M-7 ceramics and other corundum materials. They can be introduced as well in the course of crushing, milling, and mixing. The co-

loring effect of impurities in porcelain and ultraporcelain materials is neutralized by a great amount of vitreous phase, in which the relative content of the coloring impurities is not high, whereas in high-alumina materials containing a lower amount of vitreous phase, the impurities have a significant effect on the tint of ceramics and refractories.

Therefore, in production of corundum ceramics it is essential to use only the purest possible initial components not containing colorant impurities and to exclude contamination of ceramic batches and mixtures with undesirable impurities in the course of production. The damaging effect of impurities is manifested not only in tinting of ceramics but also in impairment of their thermomechanical and electric parameters. The impurities cause a substantial nonisometric growth of corundum grains due to the processes of crystallization and recrystallization.

The negative effect of impurities can be eliminated by introducing small quantities of additives (0.05 – 1.50%) of magnesium and yttrium oxides, which delay the growth of corundum grains and ensure the production of ceramics with a fine-crystalline structure and good thermomechanical properties [7]. In this case corundum ceramics can have better whiteness and even clarity, as happens when even 0.2% MgO is added to alumina after firing of the ceramics in a hydrogen medium (Polikor, Kador).

Alumina of nearly all grades (GOST 30559–98) contains the above listed impurities in an amount sufficient for tinting of corundum ceramics.

To remove Na₂O impurities, up to 1% boric anhydride is introduced in alumina and forms volatile compounds with sodium oxide, which evaporate during preliminary firing of alumina at a temperature not less than 1450°C [10]. However a complete removal does not take place, and the material is additionally contaminated with boron, which even in small quantities (0.001%) can cause a significant growth of corundum grains.

In subsequent milling, various impurities may be introduced in alumina that are usually washed off with hydrochloric acid. Milling of alumina in rubberized mills may result in adding organic and carbonaceous impurities, which in firing can cause reduction of oxides.

One of the intensely colorant oxides is TiO₂ (or more exactly, lower titanium oxides and metallic titanium), whose quantity in alumina is not regulated. The gray, violet, or black tint of corundum ceramics is frequently determined by the formation of solid solutions of Ti³⁺ in Al₂O₃. In a reducing medium, TiO₂ can be reduced to metallic titanium, in the presence of carbon, to titanium carbide, and in the presence of nitrogen, nitrides and carbonitride phases can be formed. The thermodynamic probability of their formation is very high and can occur starting with temperatures 1000 – 1300°C [11].

In addition to Na₂O · Al₂O₃, M-7 may contain calcium hexaluminates CaO · 6Al₂O₃, which is a variety of β-Al₂O₃ crystallized in a hexagonal structure and having density 3.3 – 3.4 g/cm³.

The authors of [11] consider in detail the problem of reduction of various oxides in the melting of electrocorundum and the thermodynamic probability of these processes.

An interesting study dedicated to the reaction of Al₂O₃ with TiO₂ in the sintering of corundum ceramics in a hydrogen medium with a variable dew point and in vacuum was performed by A. V. Inozemtseva [12].

It follows from the above that the problems of tinting of M-7 ceramics and other corundum materials are not yet sufficiently investigated and the reasons for tinting are not revealed. Apparently, tinting of ceramics M-7 is related to impurities, which are concentrated in the binding vitreous phase and in β-Al₂O₃.

In view of the formation of a gray tint in firing corundum ceramics in a reducing medium and its transition to a yellow tint after heat treatment in an oxidizing medium, it can be assumed that this is caused by the presence of iron impurities.

Consequently, in the production of M-7 ceramics, it is necessary to pay close attention to monitoring of iron impurities, which can be accomplished using chemical and spectral analysis.

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